Ultra-Sensitive and Quantitative Profiling and Imaging of Dopants and Impurities in Semiconductors

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1. Introduction

We have built a new analytical time-of-flight (TOF) instrument capable of sputter-initiated resonance ionization microprobe (SIRIMP) [1,2] measurements. This instrument has the ability to obtain quantitative element concentration depth profiles and images with very high depth resolution and virtually no matrix effects. The SIRIMP technique is especially valuable for ultratrace element analysis in samples where the complexity of the matrix is a serious source of interferences.

2. Experiment

In the SIRIMP experiments, the sample is bombarded with a high energy pulsed O_2^+ or Ar^+ ion beam (up to 5×10^6 ions/pulse). The expanding cloud of sputtered material consists of neutral atoms, molecular fragments, and ions; the ions are removed by timed extraction voltage switching and electrostatic energy analysis (positive ions are suppressed, negative ions are accelerated). The remaining neutral particles are then probed by the RI laser beams that ionize all the atoms of the selected element within the volume intersected by the laser beams and are then detected with a TOFMS (for more detail see [1,2]).

3. Results and Discussion

We have measured the dynamic depth profile range of ^{63}Cu implanted in silicon with 50 keV, 1×10^{14} atoms/cm^2 as a function of raster size and bombarding elements. With raster sizes of approximately 0.2 x 0.4 mm, 0.4 x 0.8 mm, 0.8 x 1.6 mm, and 1.2 x 2.4 mm, we obtained a dynamic range of better than five orders of magnitude. No significant differences were observed for dynamic range and depth profile width when using an Ar^+ ion beam instead of an O_2^+ ion beam for sputtering. Figure 1 shows a typical depth profile of ^{63}Cu and ^{65}Cu in silicon. Since a TOF instrument was used, both Cu isotopes could be monitored simultaneously. For depth profiling, a 10 keV, 1 µA O_2 ion beam was used. This Cu depth profile was taken with a raster size of approximately 0.4 x 0.8 mm. Both the experimentally determined

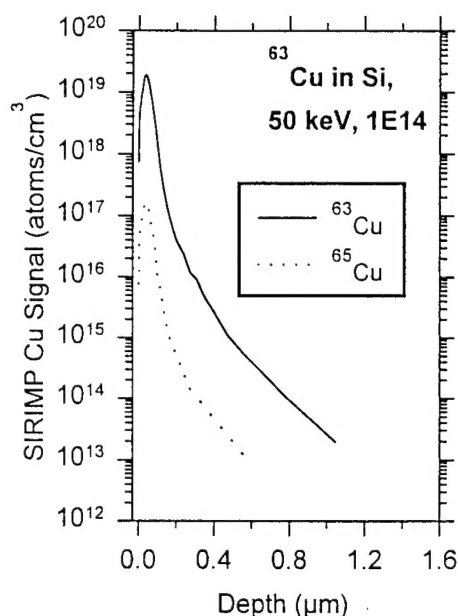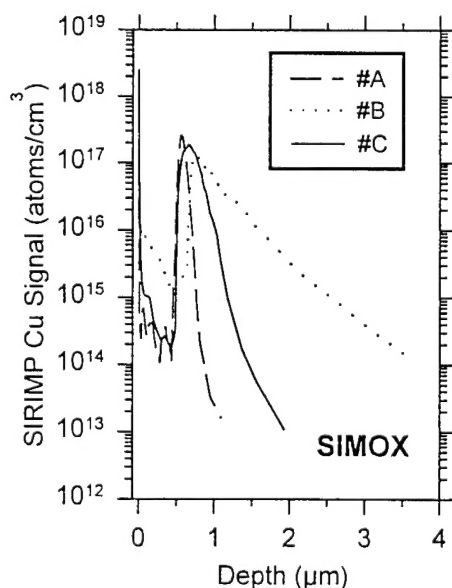**Figure 1.** Depth profiles of ^{63}Cu and ^{65}Cu in silicon.

Figure 2. Depth profiles of ^{63}Cu in SIMOX samples.

peak concentrations and the position of the profile peaks are in good agreement with those calculated using TRIM89, demonstrating the high instrumental accuracy possible with SIRIMP. The trailing edge of the profile was broadened as a result of channeling effects. The dynamic range for ^{63}Cu is better than six orders of magnitude. Due to the limited mass discrimination of the implanter, the ^{65}Cu signal is approximately 100 times lower than ^{63}Cu. The trailing edge of the profile at a concentration of approximately 2×10^{13} atoms/cm^3 (400 ppt) is still decreasing while the ratio between ^{63}Cu and ^{65}Cu is getting smaller because of natural Cu contamination in silicon. Using implant standards or samples with known concentrations, the useful yield defined as atoms detected/atoms sputtered for each ion pulse can be readily determined by measuring the signal (detected ion/pulse), the number of primary ions per pulse, the sputtering yield, and the ionization efficiency ($\sim 100\%$). The useful yield for Cu in silicon was ~4%, and the detection limit was much lower than 400 ppt.

Figure 2 shows concentration profiles of Cu contamination in three SIMOX samples. Sample A and C were SIMOX samples with a surface Si layer about 0.2 μm thick on top of a buried oxide about 0.4 μm thick. Sample B was a SIMOX sample with a surface oxide about 0.1 μm thick, a Si layer below the oxide about 0.2 μm thick, and a buried oxide about 0.4 μm thick. High Cu concentrations can be observed near the SiO$_2$/Si interface. These samples were implanted with O$_2$ at elevated temperature and then annealed in a silicon carbide tube at almost 1600 K. Probably Cu contamination was transported from the silicon carbide tube through the gas environment into the sample. From there it diffused rapidly through the top silicon and buried SiO$_2$ layers and accumulated near the back interface, probably in the form of precipitates that decorate the residual damage from the high-dose oxygen implant. No discernable matrix effects were observed at the Si/SiO$_2$ interfaces.
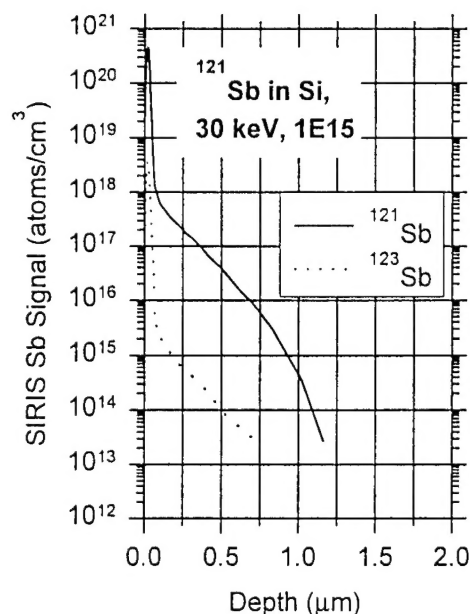
Figure 3. Depth profiles of ^{121}Sb and ^{123}Sb in silicon.

The Cu data show that laser resonance postionization is a very quantitative and matrix independent technique. This is in agreement with previously obtained B in Si data [3] and B in Si/SiO$_2$ by DeBisschop et al. [4]. The above described data are obtained with one sacrifice: each depth profile can be obtained only for one specific element. In future experiments, however, SIRIMP can be interleaved with SIMS or nonresonant ionization techniques, thus allowing simultaneous monitoring of major constituents such as Si$^+$ and SiO$^+$ as a function of depth.

Figure 3 displays a SIRIMP Sb depth profile obtained from a silicon sample implanted with 30 keV, 1x10^{15} atoms/cm^2. The samples were analyzed with a 10 keV O$_2^+$ primary ion beam and a raster area of approximately 0.8 x 1.6 mm which was reduced to 0.4 x 0.8 mm after the signal of the trailing edge decreased by a factor of 8000. The ^{121}Sb signal is approximately 100 times lower than ^{123}Sb. The typical analysis time was between 30 minutes to reach five orders of magnitude and 2 to 3 hours to reach seven orders of magnitude. The analysis time could be significantly reduced by using smaller raster areas, less data points, and/or higher repetition rate lasers. The trailing edge of the profile at a concentration of approximately 2x10^{13} atoms/cm^3 (400 ppt) is still decreasing while the ratio between ^{121}Sb and ^{123}Sb is getting smaller, probably because of natural Sb contamination in silicon. The useful yield was ~3% and the detection limit for the Sb SIRIMP measurement was less than 5x10^{12} atoms/cm^3.

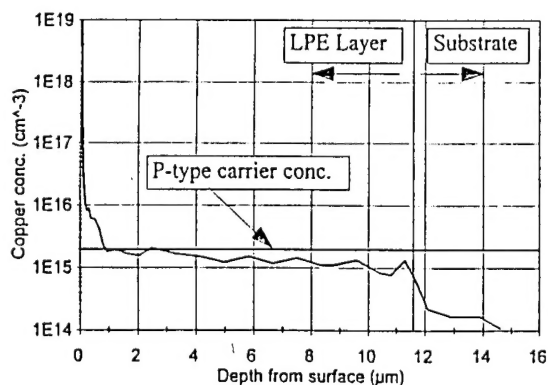SIRIMP was also applied to measure Cu contamination in HgCdTe (MCT) samples. Figure 4 shows a typical example of such a depth profile extending through an anomalous p-type MCT liquid phase epitaxy layer into the substrate. The p-type carrier (hole) concentration measured on the same sample is also shown in the figure for reference. In the bulk of the layer, the copper concentration is about equal to the net hole concentration. The large spike of Cu, indicated at the surface of the sample, is typical of many of the samples and is independent of the Hall results. This surface contamination is probably due to incomplete
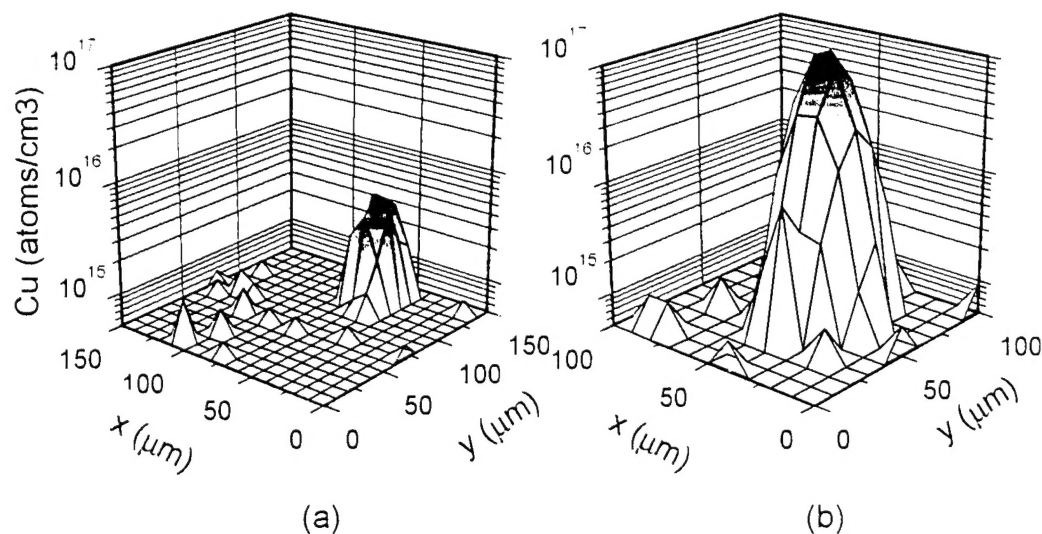

Figure 4. Depth profile for Cu in an anomalous p-type HgCdTe film.

Figure 5. SIRIMP images of copper concentration around (a) tellurium and (b) cadmium inclusions.

cleaning when the indium contacts were removed after Hall testing. The data also shows clearly that the Cu concentration in the substrate is about ten times lower than the MCT film, typical of the p-type films measured in this study. From this and other obtained data it could be concluded that Cu is nearly 100% electrically active and that it is solely responsible for anomalous p-type conversion problems in these films.

Figure 5 shows SIRIMP images of copper concentration around Te and Cd inclusions in an CdZnTe (CZT) film. It is clear from the images that the copper concentration is approximately 10 times higher in the Te inclusion than in the surrounding CZT matrix and approximately 500 times higher in the Cd inclusion. These data support the theory that the copper preferentially migrates to Te/Cd second phase regions inside the CZT matrix. Further experiments have to be performed to verify whether the solubility of Cu is much higher in Cd than Te.

[1] H.F. Arlinghaus, T.J. Whitaker, C. F. Joyner, P. Kwoka, B. Jacobson, and J. Tower, see this proceedings.

[2] H.F. Arlinghaus and C.F. Joyner, J. Vac. Sci. Technol. **B14 (1)**, 1996, in press.

[3] H.F. Arlinghaus, M.T. Spaar, N. Thonnard, A.W. McMahon, T. Tanigaki, H. Shichi, and P.H. Holloway, J. Vac. Sci. Technol. **A11**, 2317 (1993).

[4] P. DeBisschop, J. Gomez, and W. Vandervorst, see this proceedings.